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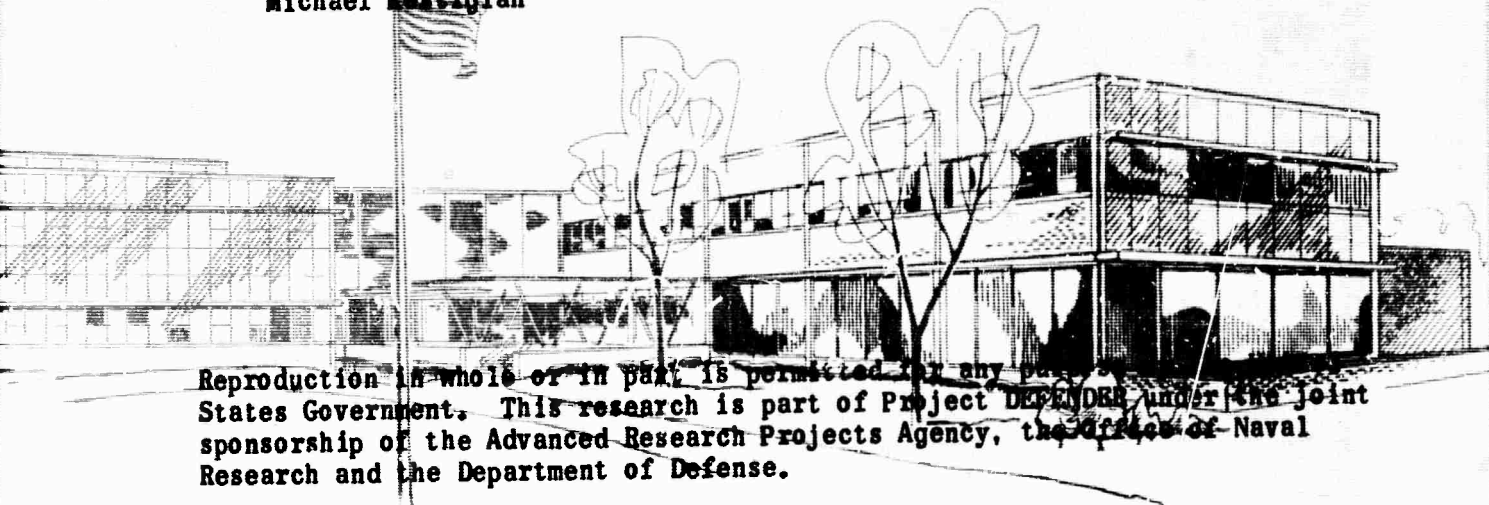# FLUORESCENT ION INTERACTION

## IN LASER CRYSTALS

### SEMIANNUAL TECHNICAL SUMMARY REPORT

(For the period ending 31 May 1967)

Contract No. N00014-67-C-0266
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# SPERRY RAND RESEARCH CENTER

## SUDBURY, MASSACHUSETTS

# FLUORESCENT ION INTERACTION IN LASER CRYSTALS

## Abstract

Factors influencing the fluorescence of the neodymium ion in garnet crystals (especially $Y_3Al_5O_{12}$) are being investigated in order to improve the laser characteristics of these materials. In order to increase the doping levels of the active ions, the effect of compensating ions on the concentration of neodymium ions for given growth conditions is being investigated. Possible deleterious effects in the optical properties of the active ion in the presence of these compensating ions are also being studied. The use of energy transfer to enhance the fluorescence of the neodymium ion has been considered. Energy transfer from the cerium ion to the neodymium ion has been observed. In a collateral study, the optical properties of the cerium ion in garnet crystals have been extensively investigated. Methods of improving the efficiency of the energy transfer in these materials have been considered.

# I. SUMMARY

During the reporting period ending 31 May 1967, studies were conducted on the factors affecting the fluorescence characteristics and, therefore, the laser characteristics of the neodymium ion in garnet host materials. Compensating ions have been used to increase the concentration of active ions in $Y_3Al_5O_{12}$. It has been found that the optical properties, such as the fluorescent transition linewidth, may be influenced by the incorporation of additional ions. Energy transfer from a sensitizing ion to the active ion (i.e., $Nd^{3+}$) have been used to enhance the active ion fluorescence. The transfer of energy from the cerium ion to the neodymium ion has been observed and the optical properties of the cerium ion have been investigated.

The use of compensating ions has been found to increase the concentration of neodymium ions in $Y_3Al_5O_{12}$. When large concentrations of compensating ions are used the optical properties may be altered and a broadening of the optical transition may be observed. The broadening of the optical transitions is especially prominent when a large compensating ion such as the $Gd^{3+}$ ion in the $Y^{3+}$ site or the $Ga^{3+}$ ion in the $Al^{3+}$ site is used to expand the average lattice parameters. The substitution of a smaller ion such as $Lu^{3+}$ in $Y^{3+}$ site to compensate for the larger $Nd^{3+}$ ion has been shown to minimize the broadening effects.

In an effort to increase the pumping efficiency of the excitation lamp, sensitizing ions have been used. Energy transfer has been observed from the cerium ion to the $Nd^{3+}$ ion in $Y_3Al_5O_{12}$. The optical properties of the cerium ion in garnet hosts have been studied because of certain anomalous features of these properties. Problems which limit the

usefulness of energy transfer in these materials have also been considered.

## II. COMPENSATING ION EXPERIMENTS

One of the major problems associated with the inclusion of the neodymium ion in $Y_3Al_5O_{12}$ is the relatively low concentration of active ions which can be incorporated into the Czochralski-grown crystals. We have been unable to prepare crystals of $Nd_3Al_5O_{12}$ by any method. Thus there is an intermediate solution of $Y_3Al_5O_{12} - Nd_3Al_5O_{12}$ which produces the maximum concentration of the $Nd^{3+}$ ion possible. The difficulty of the ion incorporation may be alleviated, but not solved, by extremely slow growth rates. A further difficulty arises from the appearance of core strains which are caused by or accentuated by the doping ions. The problem appears to be the result of the discrepancy in size between the $Nd^{3+}$ ion and the $Y^{3+}$ ion which it replaces in the $Y_3Al_5O_{12}$ crystal. The total effect may indeed have some advantages. The large size of neodymium ion apparently causes a repulsion between the oversized active ions, e.g., through crystal strain, and the ions tend to remain the maximum distance apart consistent with the concentration. That is, there is not a random distribution of active ions. This may serve to minimize the magnitude of the non-radiative interactions between the neodymium ion. This result would be consistent with additional effects which have been observed in the transfer of energy.

Two solutions have been considered to increase the concentration of neodymium ions and to facilitate active ion assimilation during the growth of $Y_3Al_5O_{12}$ doped with neodymium. The first solution would be to

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expand the average lattice parameters by the inclusion of larger ions in the yttrium site or in the gallium site. Although substitution in either site is possible, there appears to be the fundamental limitation that too large an ion or too heavy a concentration substituted in the $Y^{3+}$ ion site will not allow formation of crystals, (e.g., as was pointed out with $Nd_3Al_5O_{12}$). On the other hand, the substitution in the aluminum site by a larger ion is more promising because it is found that crystals in the entire range of solid solutions of $Y_3Al_5O_{12} - Y_3Ga_5O_{12}$ can be formed.

The second possibility for increasing the concentration of neodymium ions is to attempt to compensate for the large size of the neodymium ion by an ion smaller than the yttrium ion. The physical picture would be that the lattice strains caused by the oversized neodymium ion would be relieved by the smaller ions.

Both of these methods have been tried and indeed both appear, from samples prepared from the flux melt method, to increase the concentration. These crystals were found to contain flux ions, however, and therefore the results are not clear-cut, since the flux inclusion may act as a compensation ion. Preliminary results with pulled crystals indicate that the addition of the $Lu^{3+}$ ion does in fact permit a larger concentration of neodymium ions to be incorporated for given growth conditions. An additional benefit which results from this type of compensation could be the diminuation of the so-called "propeller"-type cores which are observed in Czochralski-grown, neodymium-doped $Y_3Al_5O_{12}$ crystals.

One additional effect however is observed with the use of compensating ions. Figures 1 and 2 show the room temperature fluorescence
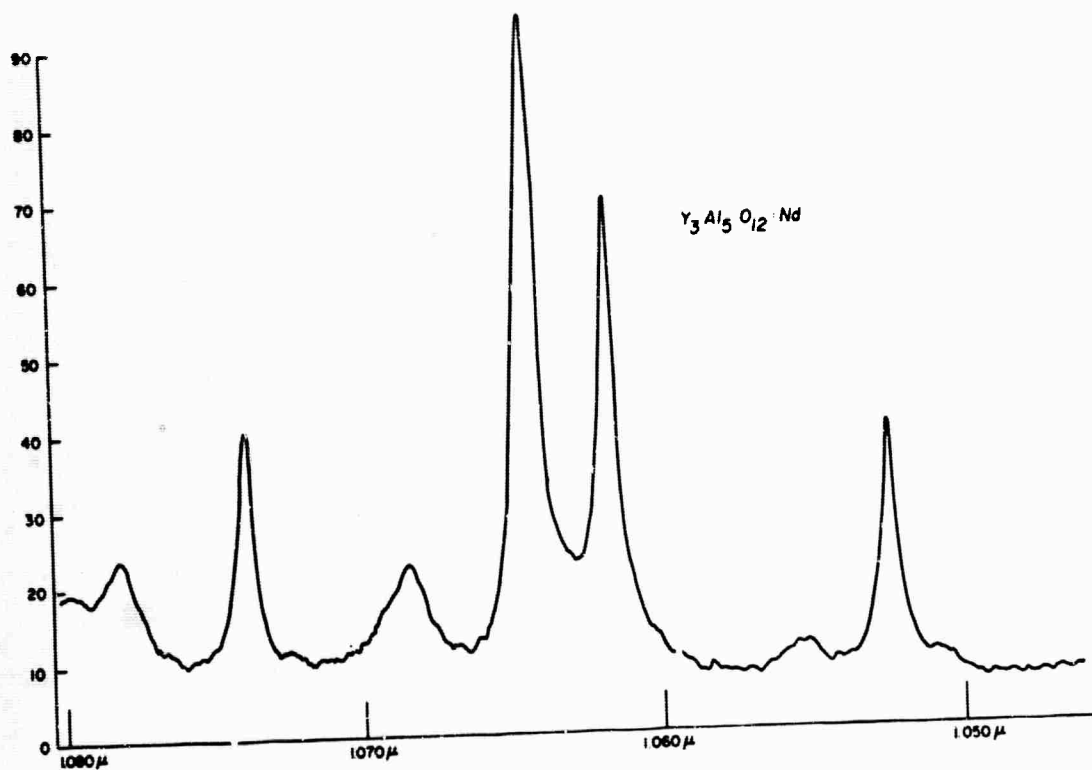
FIG. 1  The spectrum of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ fluorescent transitions of the $Nd^{3+}$ ion in $Y_3Al_5O_{12}$ measured at room temperature.
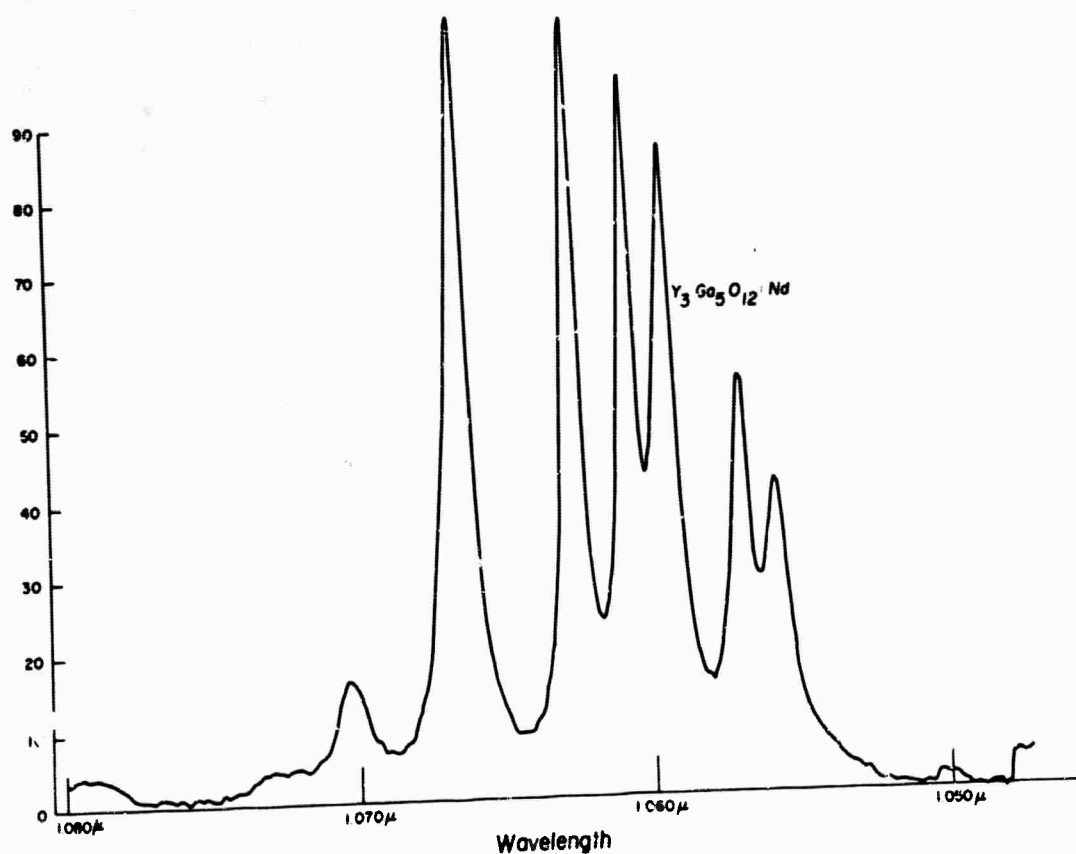


FIG. 2  The spectrum of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ fluorescent transitions of the $Nd^{3+}$ ion in $Y_3Ga_5O_{12}$ measured at room temperature.

spectra of $Y_3Al_5O_{12}$:Nd and $Y_3Ga_5O_{12}$:Nd, respectively, for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition. In Fig. 3, the fluorescence spectrum of this transition for mixed crystals of $Y_3Al_5Ga_3O_{12}$:Nd is shown. Here the linewidth of the transitions is seen to be considerably broadened. This effect is seen for other lattice-expanding, or oversized, ions. This fluorescence broadening would of course be detrimental to the characteristics for stimulated emission. In Fig. 4 is shown the fluorescence spectra for the room temperature $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition in $Y_{1.5}Nd_{.75}Lu_{.75}Al_5O_{12}$:Nd. This broadening does not appear nearly as pronounced in the case of the smaller compensating ion. These experiments were performed with flux-grown crystals. The effects of the flux material inclusions in the lattice are still under investigation.

## III. ENERGY TRANSFER

The use of energy transfer to lower the threshold for stimulated emission is a well-known technique. We have previously demonstrated energy transfer from the cerium ion to the neodymium ion in $Y_3Al_5O_{12}$ crystals. Because of certain anomalous features in the optical properties of the cerium ion in $Y_3Al_5O_{12}$, these properties were studied in detail and are discussed in Appendixes A and B. In addition to energy transfer from the cerium ion to the neodymium ion, the cerium ion can be used to sensitize the fluorescence of several other rare earth ions. (See Appendix B.) This energy transfer is apparently the result of radiative coupling between the fluorescent transitions of the cerium ion and the absorption transitions of the other rare earth ions. Moreover, attempts to lower the laser threshold in crystals of $Y_3Al_5O_{12}$:Ce:Nd because of the

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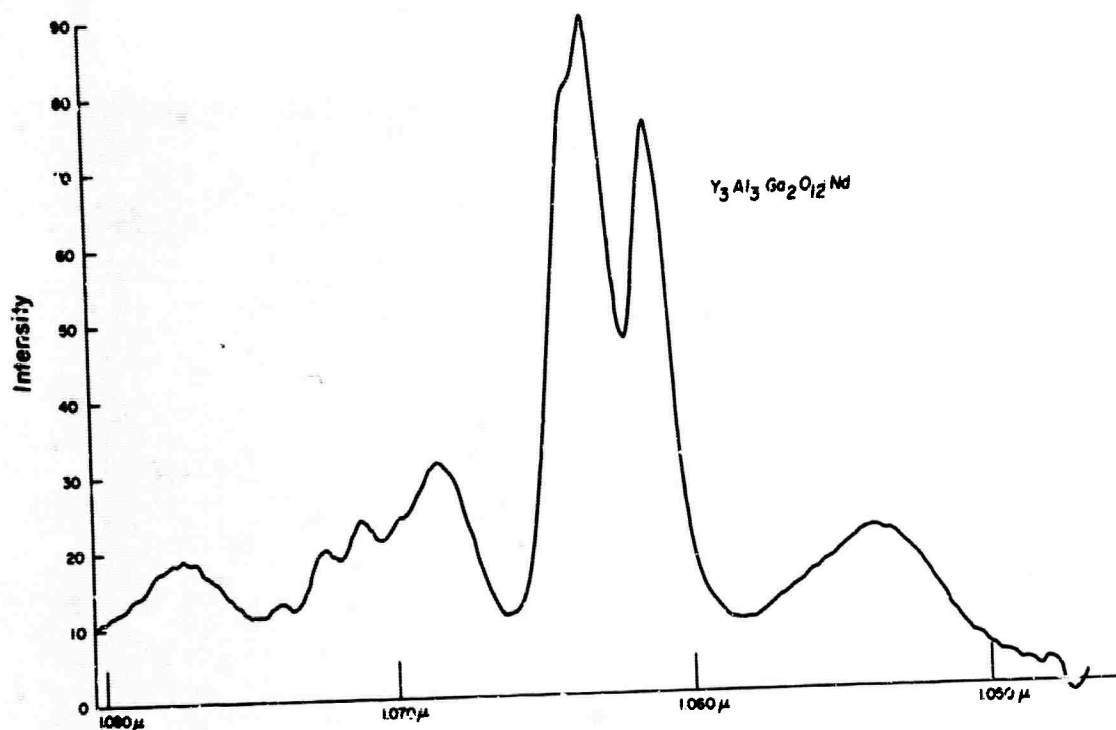
FIG. 3  The spectrum of the $^4F_{3/2} \rightarrow ^4I_{11/2}$ fluorescent transitions
of the $Nd^{3+}$ ion in $Y_3Al_3Ga_2O_{12}$ measured at room temperature.
The broadening of the major fluorescent transitions relative
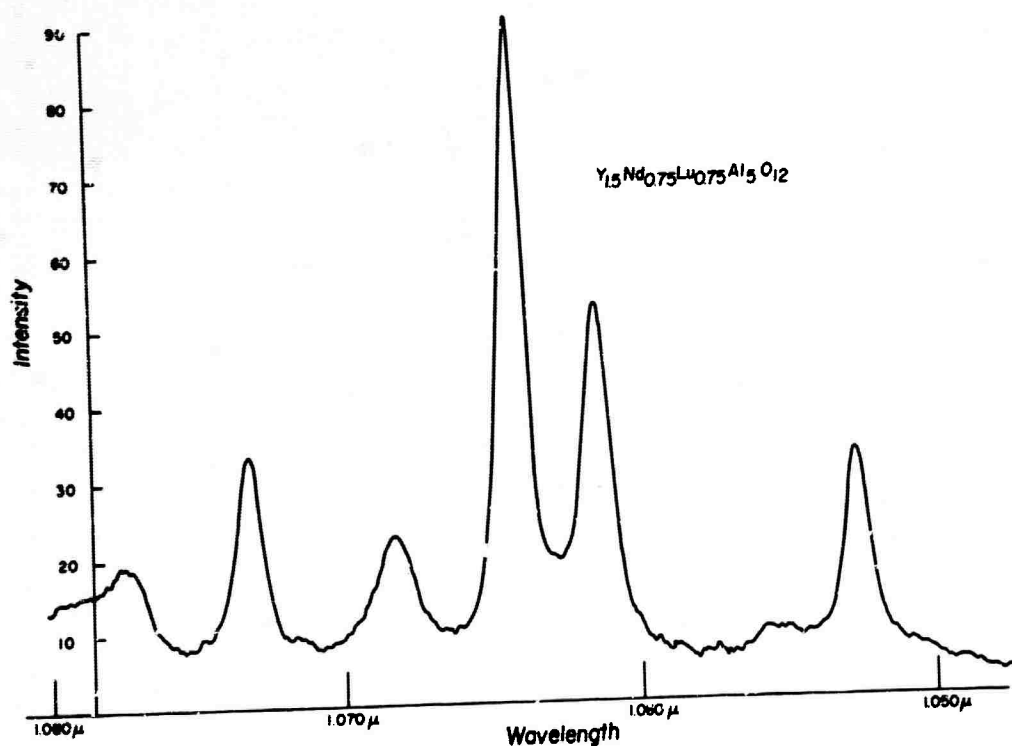to these transitions in $Y_3Al_5O_{12}$ and $Y_3Ga_5O_{12}$ is clearly
indicated.



FIG. 4  The spectrum of the $^4F_{3/2} \rightarrow ^4I_{11/2}$ fluorescent transitions of
the $Nd^{3+}$ ion in $Y_{1.5}Lu_{0.75}Nd_{0.75}Al_5O_{12}$. Some broadening of
the fluorescent transition is observed but this broadening is
not nearly as pronounced as that for the $Nd^{3+}$ ion in
$Y_3Al_3Ga_2O_{12}$ (cf. Fig. 3).

incorporation of the cerium ion have not been successful. We attribute the failure of the sensitizing ion to lower the threshold for stimulated emission to the large size of both the fluorescent ion site and the neodymium ion with respect to the yttrium ion which is replaced. As in Sec. II, these oversized ions tend to distribute themselves in such a manner as to maximize the distance to the nearest neighbor ions. A further indication of such an effect is that for given growth conditions the presence of the cerium ion reduces the concentration of the neodymium ions. Therefore the sensitization of the neodymium ion is the result of the relatively inefficient radiative transfer rather than the efficient non-radiative transfer. (A similar effect has been noted by us in previous reports for the $Cr^{3+} \rightarrow Nd^{3+}$ transfer in $Y_3Al_5O_{12}$.) Another revealing result occurred when an attempt was made to measure the excitation spectrum of the $Yb^{3+}$ ion in $Y_3Al_5O_{12}$. Although the fluorescence of the $Yb^{3+}$ ion (alone) was observed, the excitation spectrum was that due to $Nd^{3+}$ ion. We concluded that impurity amounts of neodymium ions were present and provided a very efficient transfer of excitation energy from the $Nd^{3+}$ ion to the $Yb^{3+}$ ion. Because the $Yb^{3+}$ ion is smaller than the $Y^{3+}$ ion which it replaces, the $Yb^{3+}$ ion and the $Nd^{3+}$ ion tend to cluster, consequently providing a very efficient transfer of energy.

We conclude that our previous attempts to improve the laser performance characteristics of $Y_3Al_5O_{12}$:Nd have not been successful because the effects due to ionic size have not been taken into account. Further work will be focused toward neutralizing these ion size effects through the use of compensating ions or through novel sensitizing ions.

## IV. REMARKS ON THE TWO COLOR LASER PROBLEM

In the previous sections comments have been made that the size of the active ion relative to the ion which it replaces, and the sizes of the compensating or sensitizing ions relative to the ions which they replace, influence the properties of these materials. That is, oversize active ions, such as the $Nd^{3+}$ ion in $Y_3Al_5O_{12}$, appear not to assume a random distribution, but rather tend to remain as far apart as the equilibrium grown conditions will permit. This feature, while severely limiting the concentration for given growth conditions, has the advantage of minimizing the ionic interactions. We speculate therefore that the host $Lu_3Al_5O_{12}$ would be a likely candidate in which to observe stimulated emission at two wavelengths, i.e., from two different rare earth ions, or the so-called two color laser. The $Lu^{3+}$ ion is the smallest of the rare earth ions and therefore any pair of rare earth ions substituted in the lattice would tend to remain as far apart as the growth conditions would permit. Even if the energy levels of the ions are such as to allow interactions through the relatively efficient non-radiative process, the radial dependence of such an interaction is proportional to $r^{-n}$ (where r is the average distance between the interacting ions) and this interaction would be minimized in this system. We point out that the incorporation of active ions in this small lattice would be correspondingly more difficult than the similar procedures in $Y_3Al_5O_{12}$. In spite of potential problems, we suggest that the host $Lu_3Al_5O_{12}$ would be a likely candidate in which to observe stimulated emission from two ions.

## V. FUTURE INVESTIGATIONS

During the next semiannual period ending 30 November 1967, studies will continue on efforts to improve the laser characteristics of neodymium-doped garnet crystals.

Further studies will be made to establish the effect of compensating ions on the optical transitions (particularly the linewidth) of the fluorescent transitions.

Attempts will be made to maximize the useful concentration of neodymium ions in $Y_3Al_5O_{12}$ through the use of compensating ions. Factors which will limit the useful concentration, apart from the ability of the $Y_3Al_5O_{12}$ to accept neodymium without disruption of the crystal, include optical perfection of the crystal and ionic interaction resulting in nonradiative de-excitation which cause deterioration of the fluorescence.

Similarly, attempts will be made through the use of compensating ions to increase the efficiency of energy transfer from a sensitizing ion to the active, i.e., $Nd^{3+}$, ion. Both cerium and chromium will be used as sensitizing ions.

Laser quality crystals will be grown and tested to determine the success of the use of compensating ions in increasing the laser threshold.

APPENDIX A

OPTICAL PROPERTIES OF CERIUM-ACTIVATED
GARNET CRYSTALS

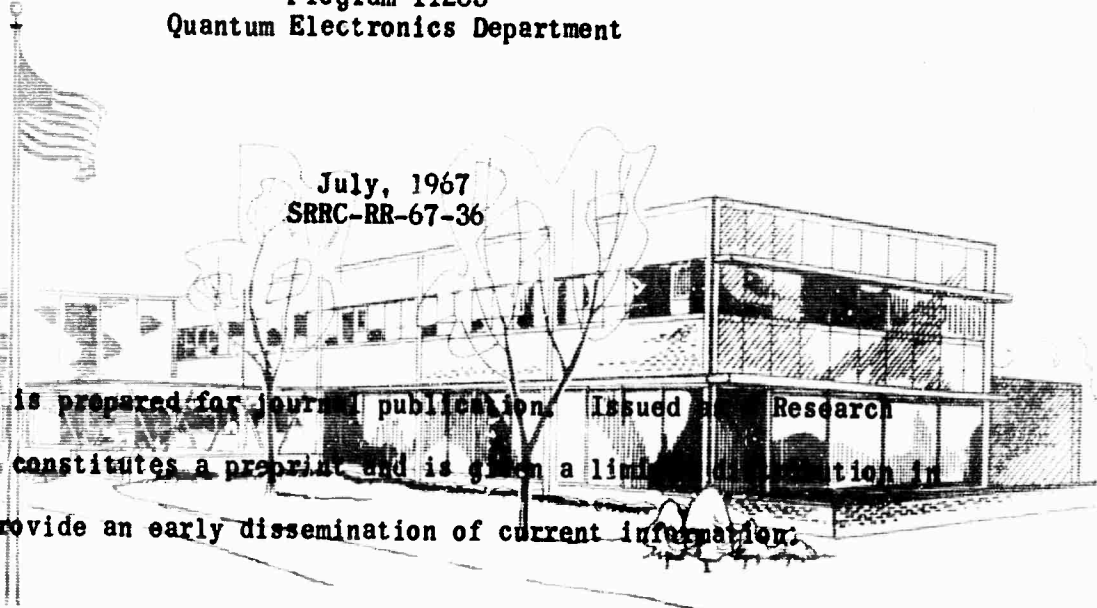(SRRC-RR-67-36)

# OPTICAL PROPERTIES

## OF CERIUM-ACTIVATED GARNET CRYSTALS

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# Optical Properties of Cerium-Activated Garnet Crystals *

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## Abstract

The optical properties of cerium-activated garnet crystals have been investigated. In the garnet crystals showing luminescence, a bright yellow fluorescence has been observed. This fluorescence exhibits structure at low temperatures, and wavelength maxima of the fluorescence spectrum profiles are found to be host-dependent. Energy transfer has been observed from the cerium ion to the neodymium ion.

## Introduction

The optical spectra of the rare earth ions in garnet crystals have been extensively investigated because of the suitability of these materials in laser applications.[1] In a previous note, we have reported preliminary data on the fluorescence of cerium-activated garnet crystals. A bright yellow fluorescence was observed in several garnet host materials. These fluorescence profiles were shown to be host-dependent, and at low temperatures the fluorescence profile was partially resolved into two components. In this paper, we report additional measurements of fluorescence spectra of the cerium ion in garnet materials. In addition, absorption data have been measured for these materials in an effort to clarify the nature of the fluorescent site.

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## Experimental

The crystals were prepared by the flux solvent method. The concentrations given for the crystals are those of the starting ingredients.[3] A Czochralski-grown, cerium-doped $Y_3Al_5O_{12}$ crystal was prepared for comparison with the flux-grown crystals.

The absorption measurements were recorded on a Beckman DK-2 Recording Spectrometer (for the visible and ultra-violet ranges) and by a Perkin Elmer 337 Grating Infared Spectrometer (for the infrared data).

The fluorescence data were taken with a Perkin Elmer 112 Recording Spectrometer with a $CaF_2$ prism. The output of the spectrometer was detected with an EMI 9995 (S-20 response) photomultiplier. No attempt was made to correct for the response of this tube.

## Results

The absorption bands observed in several cerium-doped garnet crystals are shown in Figs. 1 and 2. A pair of absorption bands are observed at approximately 2.65 $\mu$ and 2.85 $\mu$ and a second pair are observed at 420 m$\mu$ and 380 m$\mu$. In addition, an absorption line due to the flux inclusion is observed at 260 m$\mu$. The garnets with larger cell constants appear to assimilate the flux impurities easier than those with smaller lattice constants.

The fluorescence profiles of several garnet host materials containing cerium are shown in Figs. 3 through 7. Figure 3 shows the fluorescence profiles of several garnet materials taken at room temperature in crystals where there has been a partial substitution for the $Al^{3+}$ ion in $Y_3Al_5O_{12}$:Ce. The substitution of a larger ion for the $Al^{3+}$ shifts the
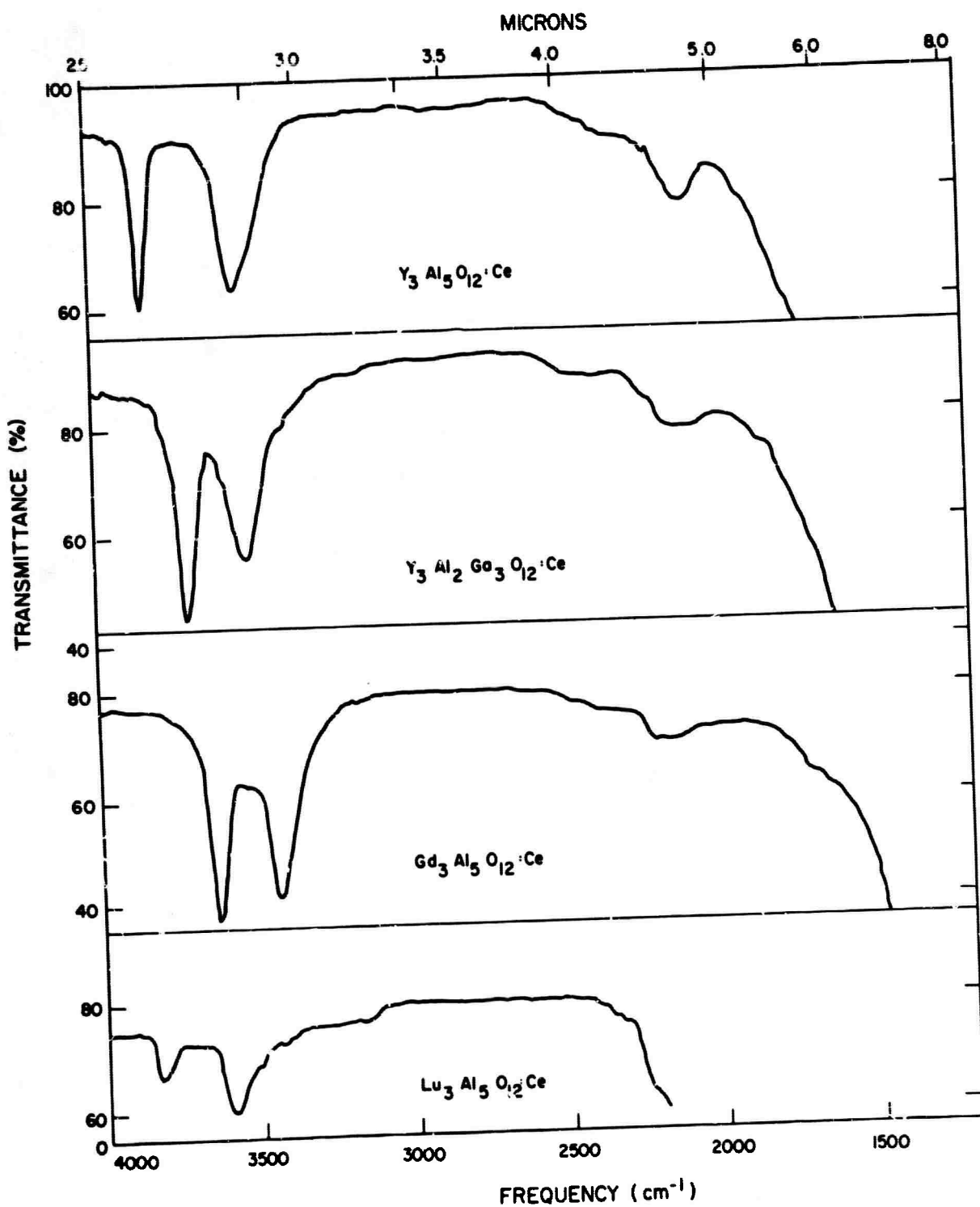
- 2 -

FIG. 1  Infrared absorntion spectra of several cerium doped garnet crystals. Two prominent  sorption transitions are observed at approximately 2.65 μ and 2.ьν μ.  The wavelength of the transition maxima vary slightly with host material.  The absorption transitions observed at approximately 4.8 μ are also observed in undoped crystals.
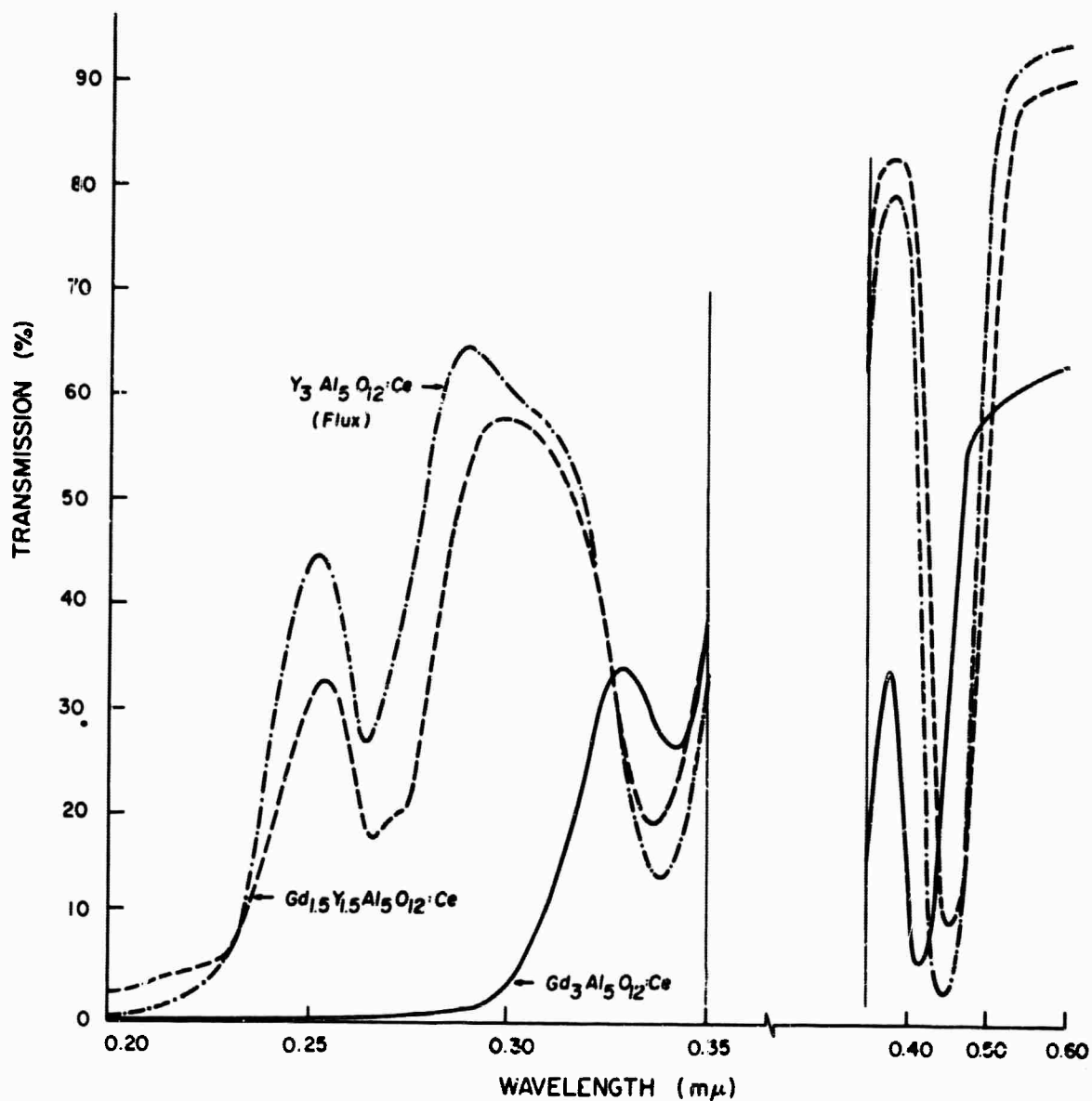
FIG. 2a  The uv absorption transitions of $Y_3Al_5O_{12}$:Ce (pulled), $Lu_3Al_5O_{12}$:Ce, and $Y_3Al_2Ga_3O_{12}$:Ce crystals. Two prominent absorption transitions are observed at approximately 420 m$\mu$ and 380 m$\mu$. An absorption transition at 260 m$\mu$, apparently due to the inclusion of flux in the crystals, is not observed in the pulled $Y_3Al_5O_{12}$:Ce sample.
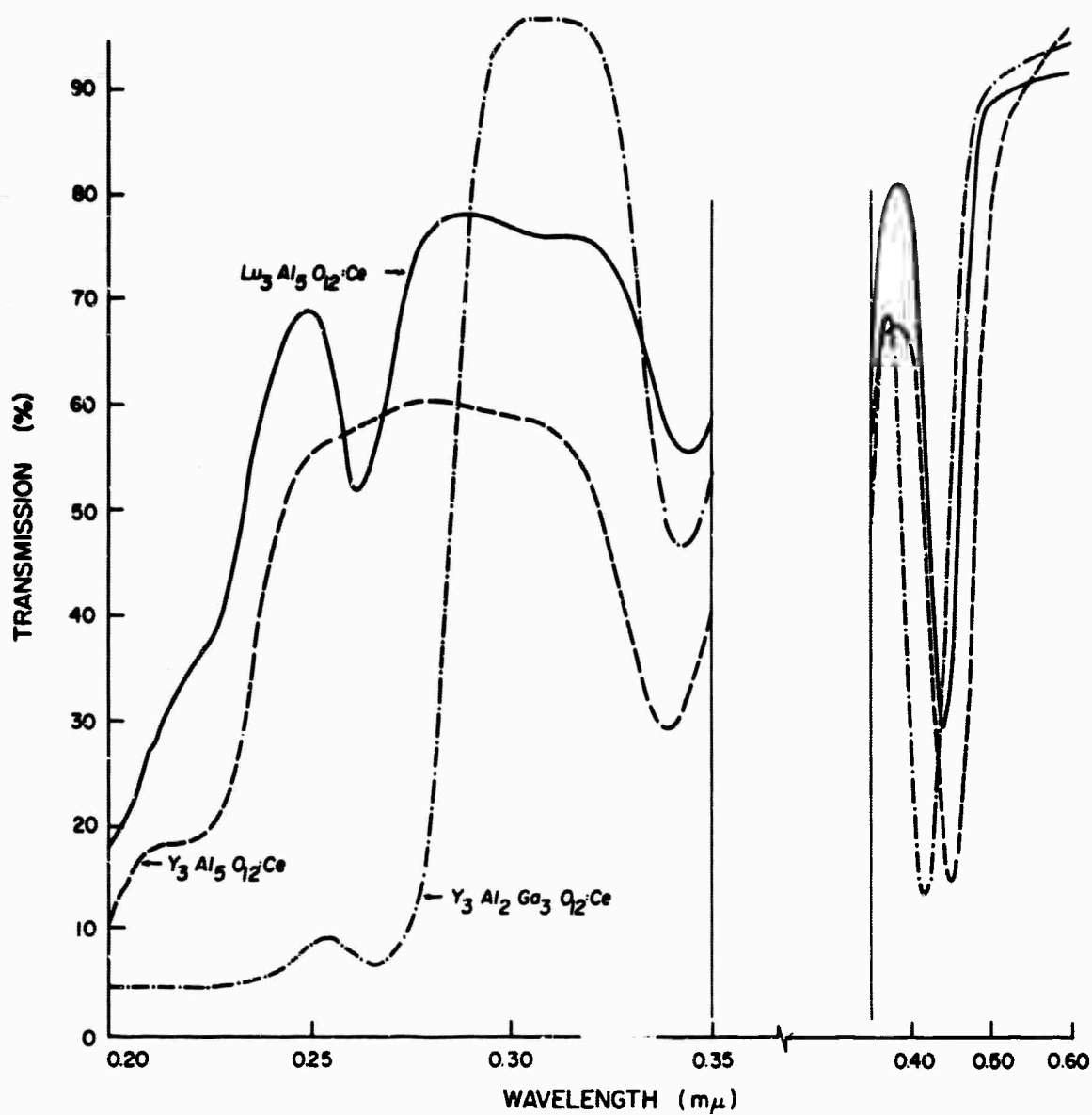
FIG. 2b   The   uv   absorption transitions of $Y_3Al_5O_{12}$:Ce (flux), $Gd_{1.5}Y_{1.5}Al_5O_{12}$:Ce, and $Gd_3Al_5O_{12}$:Ce.   Two prominent absorption transitions are observed at approximately 420 mµ and 380 mµ.   The absorption transition at 260 mµ, apparently due to the inclusion of flux in the crystals, is also observed in the flux-grown $Y_3Al_5O_{12}$:Ce samples.
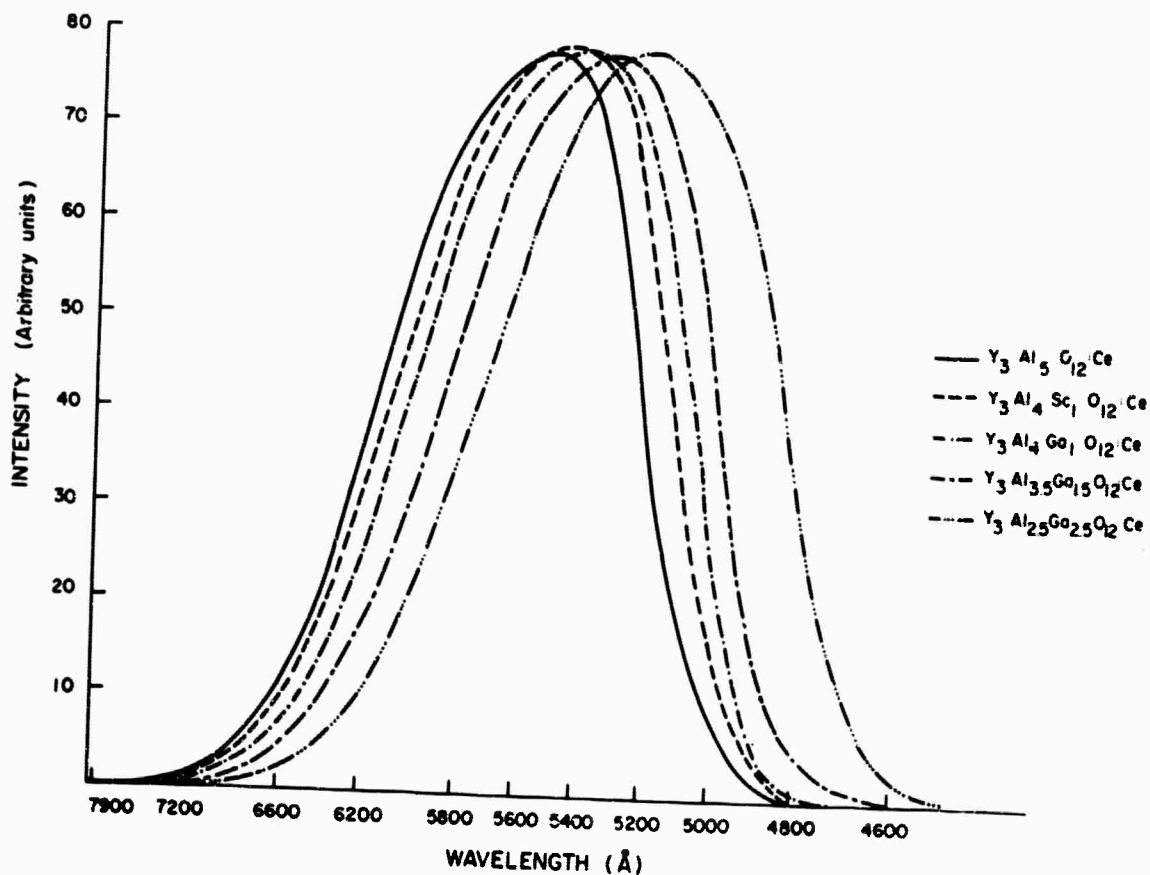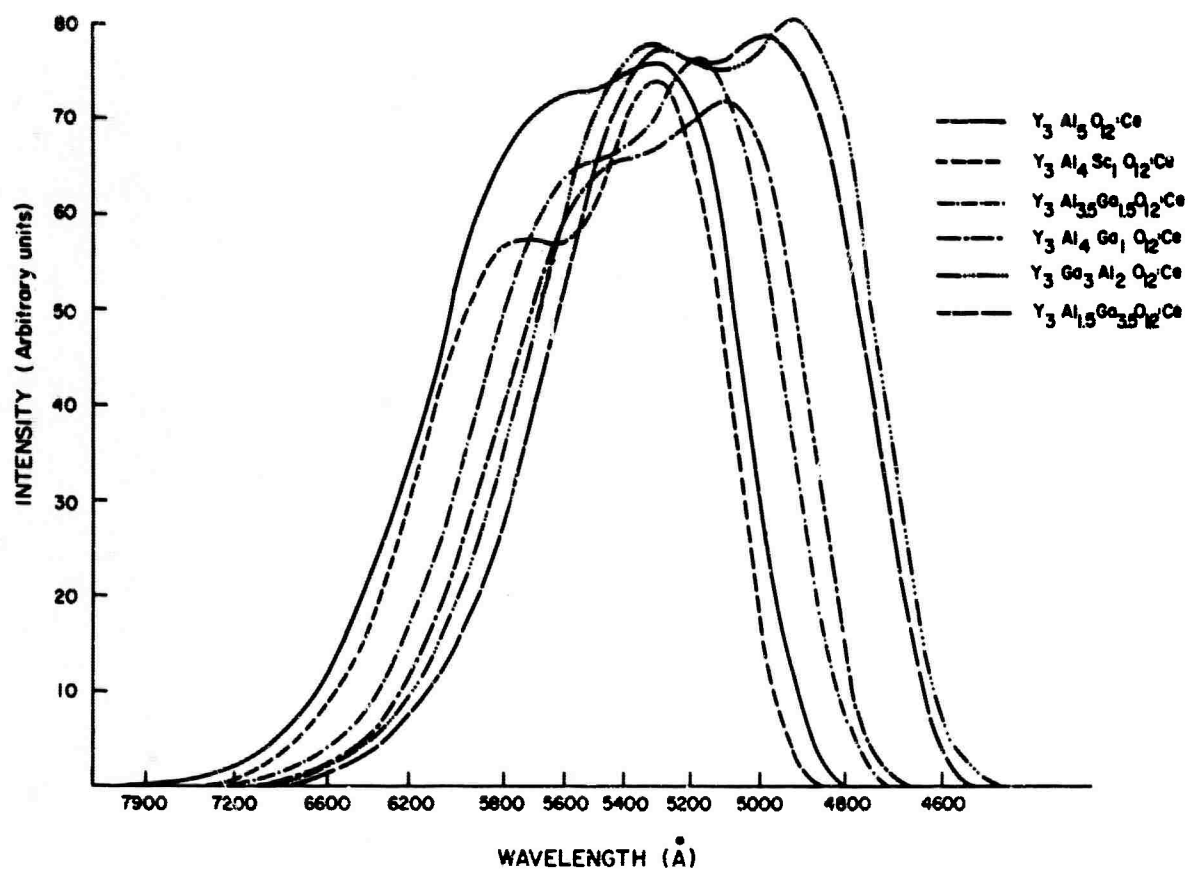
FIG. 3  Comparison of the fluorescence of cerium doped $Y_3Al_5O_{12}$ with the fluorescences observed in cerium doped garnet crystals where the $Al^{3+}$ ions have been replaced by $Ga^{3+}$ or $Sc^{3+}$ ions.  These fluorescence profiles were measured at room temperature.

INTENSITY ( Arbitrary units)

80

70

60

50

40

30

20

10

7900   7200   6600   6200   5800   5600   5400   5200   5000   4800   4600

WAVELENGTH (Å)

Legend:

— $Y_3 Al_5 O_{12}$:Ce

– – – $Y_3 Al_4 Sc_1 O_{12}$:Ce

–·– $Y_3 Al_{35} Ga_{15} O_{12}$:Ce

–··– $Y_3 Al_4 Ga_1 O_{12}$:Ce

–···– $Y_3 Ga_3 Al_2 O_{12}$:Ce

– – – $Y_3 Al_{15} Ga_{35} O_{12}$:Ce

FIG. 4  Comparison of the low temperature fluorescence of cerium doped
$Y_3Al_5O_{12}$ with the fluorescences observed in cerium doped garnet
crystals where the $Al^{3+}$ ions have been replaced by $Ga^{3+}$ or $Sc^{3+}$
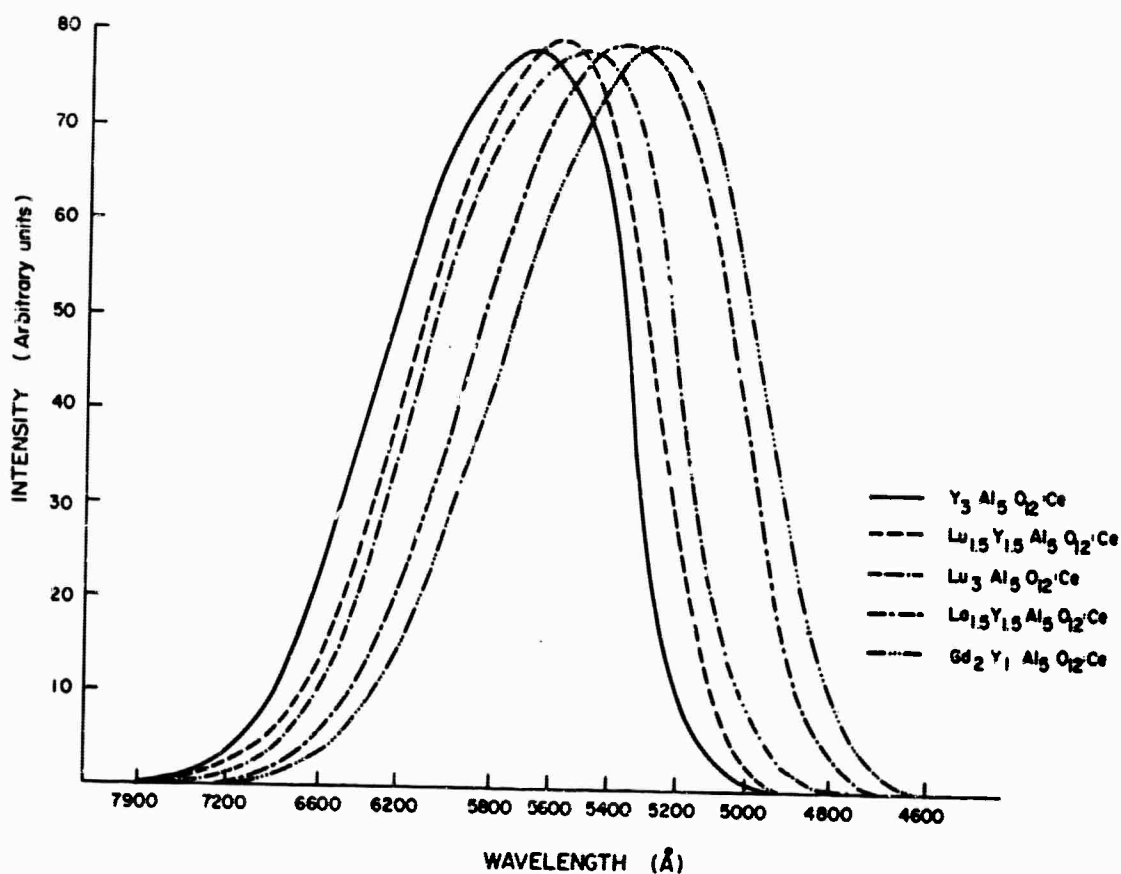ions.  These profiles were measured at $77^{\circ}K$.

FIG. 5  Comparison of the fluorescence of cerium doped $Y_3Al_5O_{12}$ with the fluorescences of cerium doped garnet crystals, where the $Y^{3+}$ ions have been replaced by $Lu^{3+}$ ions, $La^{3+}$ ions or $Gd^{3+}$ ions. These fluorescence profiles were measured at room temperature.
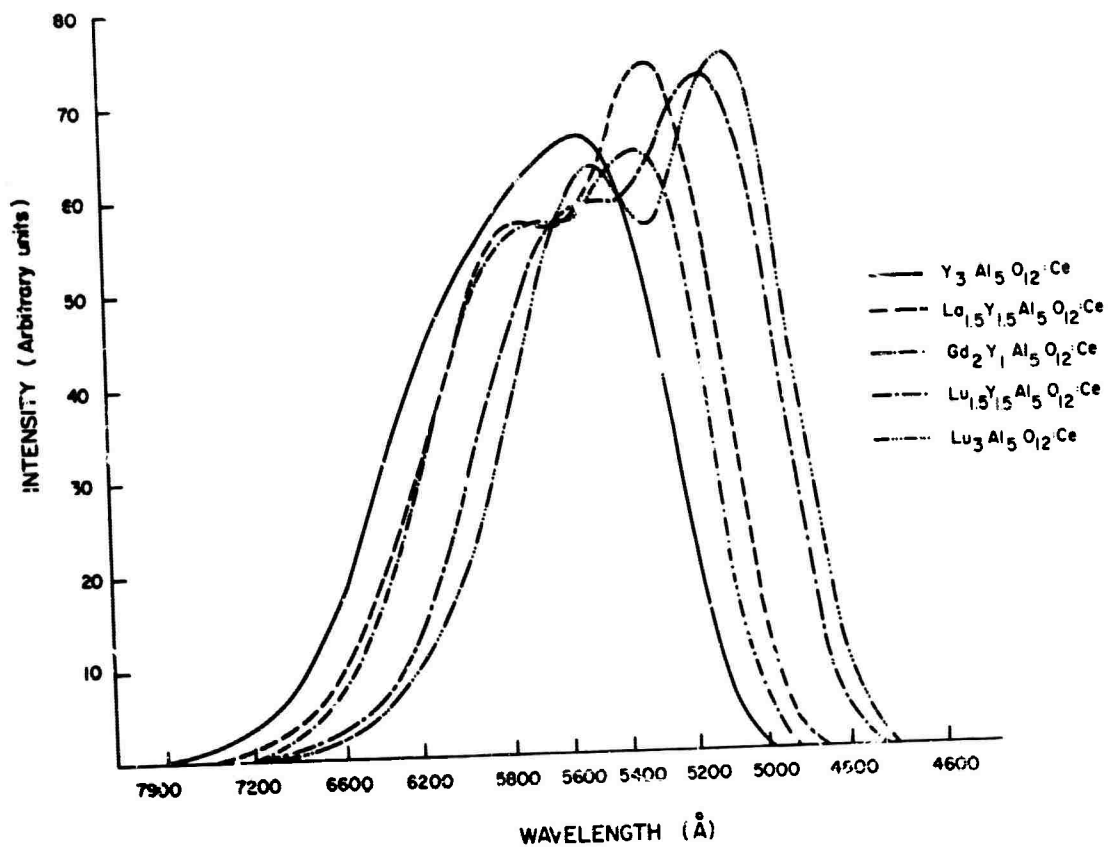
FIG. 6  Comparison of the low temperature fluorescence of cerium doped $Y_3Al_5O_{12}$ with the fluorescences of cerium doped garnet crystals where the $Y^{3+}$ ions have been replaced by $Lu^{3+}$ ions. $L$ ions or $Gd^{3+}$ ions. These profiles were measured at $77°K$.
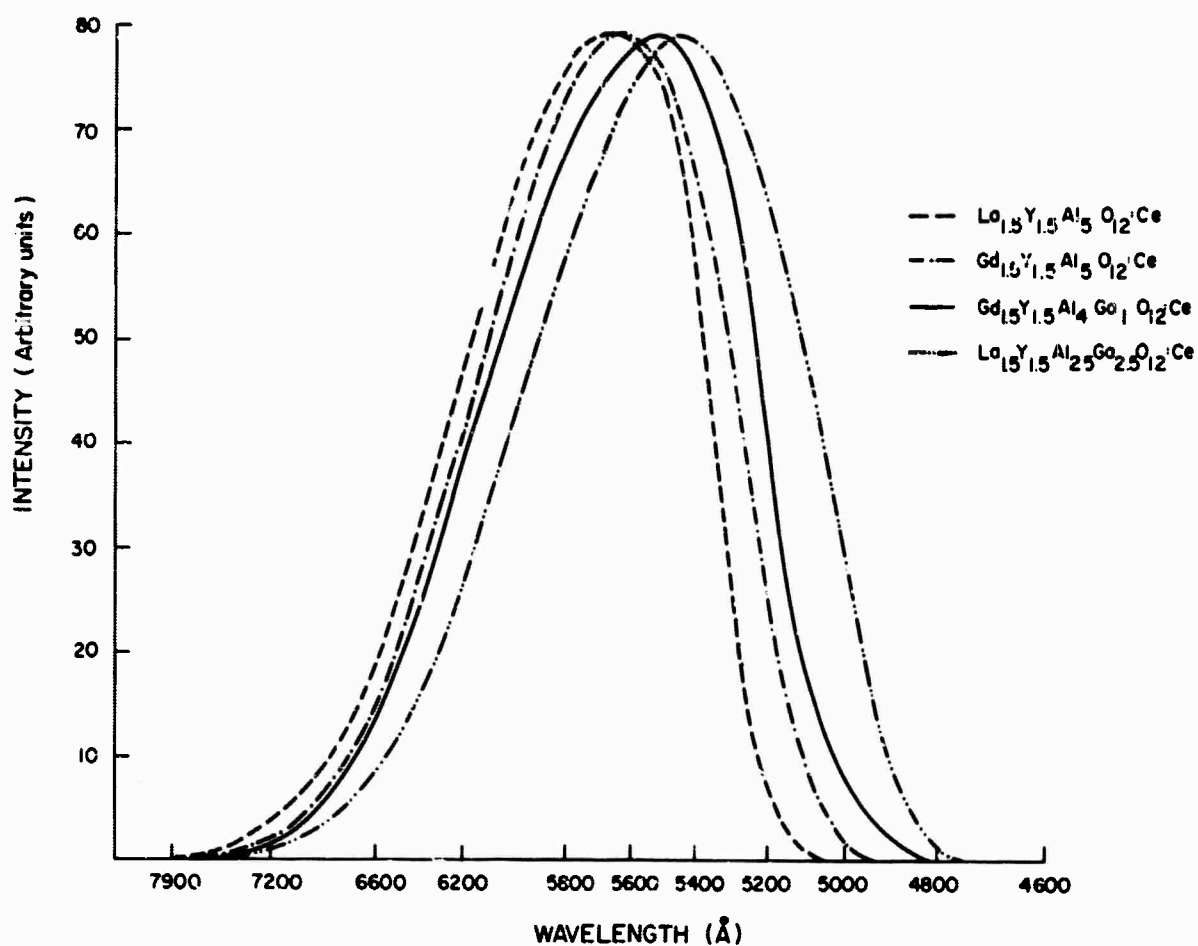
FIG. 7 Effect on the room temperature fluorescences of cerium doped garnet crystals (similar to $Y_3Al_5O_{12}$) of substituting $Ga^{3+}$ ions for $Al^{3+}$ in crystals where a partial substitution for the $Y^{3+}$ ion has already been made.

fluorescence band toward the blue. In Fig. 4 are shown fluorescence profiles of the crystals in Fig. 3 measured at low temperatures. These spectra show two partially resolved components in addition to the shift of the bands toward the blue. The fluorescence transitions are shown in Fig. 5 for crystals where a substitution for the $Y^{3+}$ ion has taken place in $Y_3Al_5O_{12}$:Ce. The substitution of the smaller $Lu^{3+}$ ion shifts the bands toward the blue while the substitution of the larger $La^{3+}$ and $Gd^{3+}$ ions shift the bands toward the red. The fluorescence profiles of Fig. 6 show the result of measuring the fluorescence transitions of the crystals of Fig. 5 at low temperature. A partial resolution of these bands into two components is again observed for some profiles. Figure 7 shows profiles where substitutions in both the $Y^{3+}$ and $Al^{3+}$ sites have taken place.

A number of other experiments have been performed on these materials. The lifetime of the fluorescence decay has been determined to be less than 1 $\mu$sec. Crystals of $Y_3Ga_5O_{12}$:Ce do not exhibit fluorescence, and the intensity of the fluorescence appears to diminish for concentration of gallium greater than $Y_3Al_2Ga_3O_{12}$:Ce. In addition, crystals of $Y_3Al_2Ga_3O_{12}$:Ce and $Y_3Al_{1.5}Ga_{3.5}O_{12}$:Ce exhibit phosphorescence which persists for several seconds after the removal of the ultraviolet excitation source.

Powder samples of these materials yield results identical to those reported above for the crystal samples when the compounds are prepared under oxidizing conditions. When the powder samples are prepared under reducing conditions, a blue fluorescence is observed, usually in addition to the yellow fluorescence. Unsuccessful attempts were made to observe structure at low temperature in this blue fluorescence component. It was not clear

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whether this structure was absent or masked by other effects, such as inter-
ference from the yellow fluorescence component.

A broadband yellow fluorescence component of the cerium ion in
these garnet materials overlaps absorption bands of several rare earth ions
of interest in laser applications, (e.g., the $Nd^{3+}$ shown in Fig. 8). This re-
sult suggests that energy may be transferred from cerium ions to the other
rare earth ion. Such a transfer is indeed found for the cerium → neodymium
as is shown by the excitation spectrum in Fig. 9. The transfer appears to
be principally composed of (the relatively inefficient) radiative transfer,
i.e., the emission of a real photon by the cerium ion and the absorption
of that photon by the neodymium ion. Because of the overlap, however, non-
radiative transfer may also take place.

## Discussion

The observed fluorescence does not appear to originate from the
$Ce^{3+}$ site. Although the low temperature structure shown in Figs. 4 and 6 is
reminiscent of the results of Kröger and Bakker,[2] and attri'uted by them to
the $Ce^{3+}$ ion fluorescence, both the absorption and fluorescence transitions
of the garnet crystals are shifted far toward the red. In addition, the
infrared absorption band of the $Ce^{3+}$ ion ($^2F_{7/2} \rightarrow {}^2F_{5/2}$), which should be
present at approximately 2200 $cm^{-1}$, is not observed. The absorption band
which is observed in this region is also found in undoped crystals and
therefore does not result from a transition of the $Ce^{3+}$ ion. The two ab-
sorption bands, which are observed in the infrared at 3500 $cm^{-1}$ and 3800 $cm^{-1}$,
cannot be idertified on the basis of the $Ce^{3+}$ energy levels. Our results
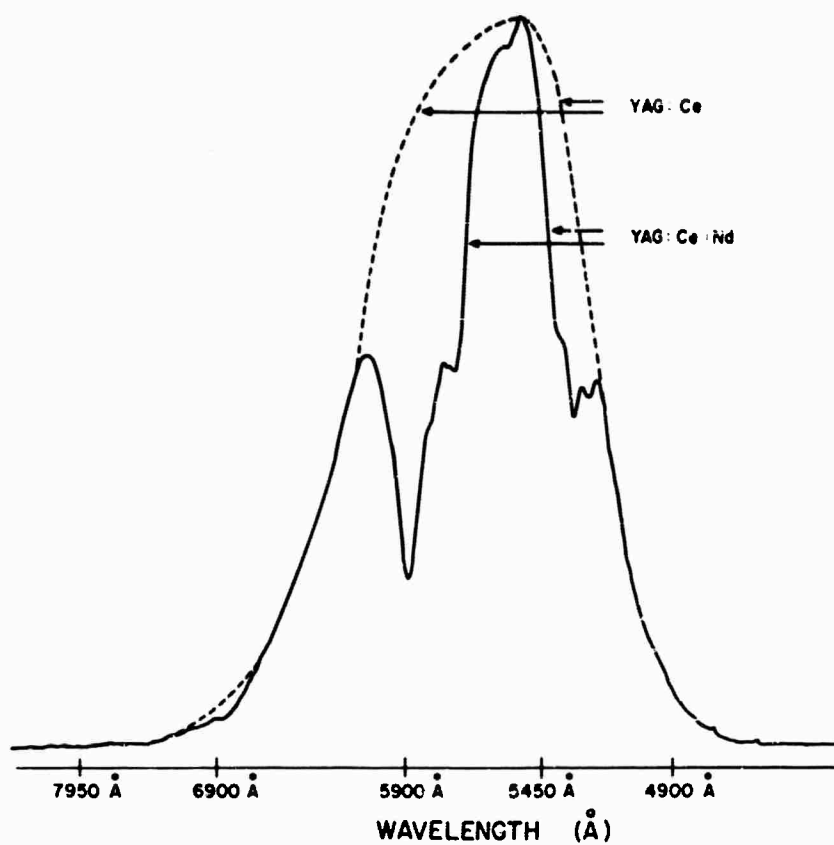with powder samples, however, do show that the cerium-doped garnet

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**FIG. 8** The comparison of the fluorescence spectra of $Y_3Al_5O_{12}$:Ce (dotted line) with $Y_3Al_5O_{12}$:Ce:Nd (solid line). The difference between the spectra in each case can be attributed to a known $Nd^{3+}$ absorption line, thereby establishing the radiative coupling between the neodymium ion and the fluorescent cerium and manganese ions.
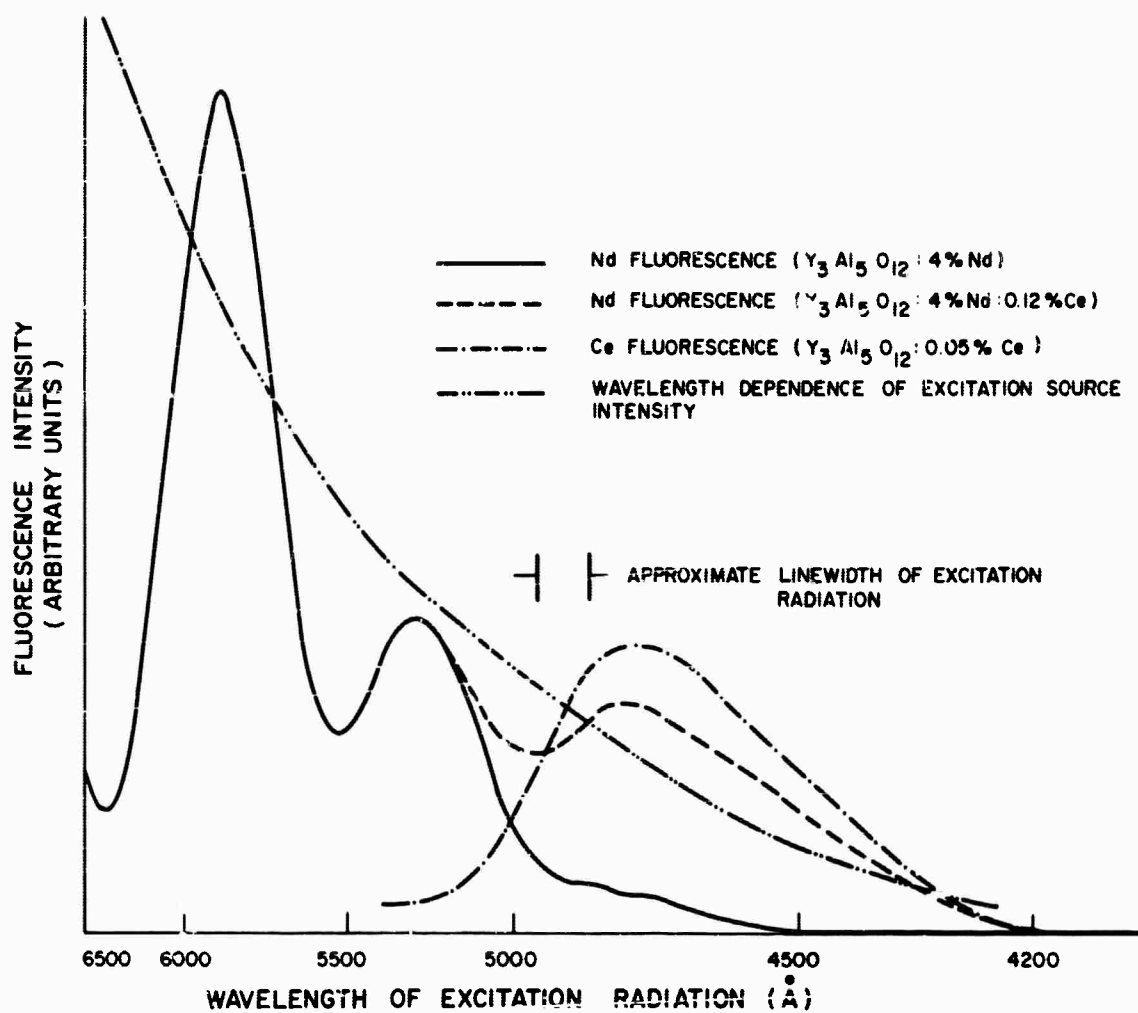
FIG. 9 Sensitization of the $Nd^{3+}$ fluorescence by the presence of Ce ion in $Y_3Al_5O_{12}$.

materials have a blue fluorescence when prepared under reducing conditions. We attribute this to the $Ce^{3+}$ ion. The yellow fluorescence, observed when the samples are prepared under oxidizing conditions, is identical to that reported above for garnet crystals, and we believe this fluorescence is due to the presence of the $Ce^{4+}$ ion. Similarly, the yellow fluorescence observed in the garnet crystal samples is the result of the presence of the $Ce^{4+}$ ion. The actual fluorescence, however, may originate from associated lattice sites needed to compensate for the valence of the $Ce^{4+}$ ion in the lattice.

The structure, which is observed in the low temperature spectrum, can be assigned to fluorescence transitions leaving the level at $\sim 420$ m$\mu$ and terminating at the levels at $\sim 2.6$ $\mu$ and $2.8$ $\mu$. The differences between these transition energies and the observed fluorescence transition energies can be identified with the Stokes shift of the fluorescence. Therefore, the replacement of $Al^{3+}$ or $Y^{3+}$ ions changes the lattice parameters determining the amount of the Stokes shift and accounts for the shifts of the fluorescence profiles observed in Figs. 3 through 7.

## Acknowledgment

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3. M. Kestigian and W. W. Holloway, Jr., *Crystal Growth* (Pergamon Press, New York, 1967), pp. 451-456.

4. F. A. Kroger and J. Bakker, Physica $\underline{VIII}$, 628 (1941).

APPENDIX B
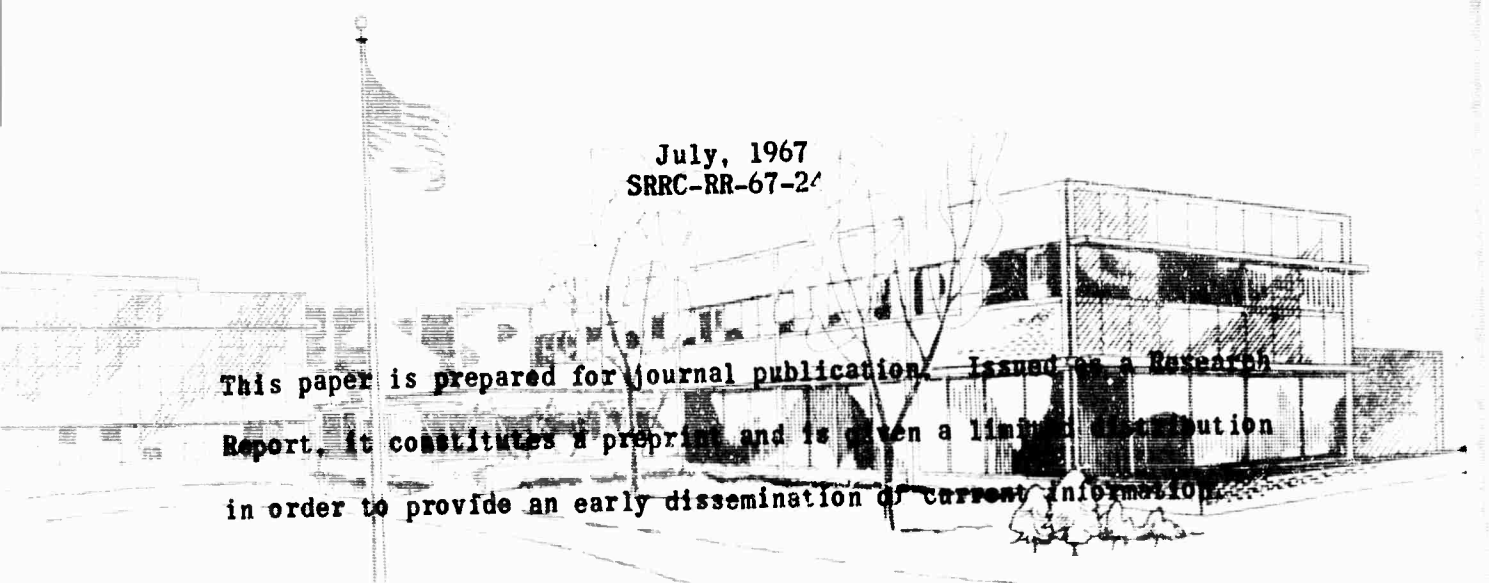
ON THE FLUORESCENCE OF CERIUM-ACTIVATED
GARNET CRYSTALS

(SRRC-R. -≁ ·24)

ON THE FLUORESCENCE

OF CERIUM-ACTIVATED GARNET CRYSTALS

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# On the Fluorescence of Cerium-Activated Garnet Crystals[*]

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The optical properties of rare-earth doped garnet materials have been extensively investigated because of the importance of these hosts in laser applications.[1]  In this note we report measurements of the fluorescence of crystals of $Y_3Al_5O_{12}$:Ce, $Lu_3Al_5O_{12}$:Ce and $Y_3Al_2Ga_3O_{12}$:Ce.  In these cerium doped garnets, a bright broadband fluorescence has been observed which exhibits doublet structure at low temperature.  This structure is reminiscent of the spectra reported by Kröger and Bakker[2] except the fluorescence is shifted toward the red.  The fluorescence profile varies with the garnet host material and this change may be easily observed by the luminescence color under uv excitation.  This fluorescence does not appear to originate from the $Ce^{3+}$ ion incorporated in these hosts.

The fluorescence spectra of $Y_3Al_5O_{12}$:Ce, $Lu_3Al_5O_{12}$:Ce and $Y_3Al_2Ga_3O_{12}$:Ce (taken at room temperature) are shown in Fig. 1.  In this figure the difference between the fluorescence spectra of the samples is clearly seen.  Under uv excitation, the fluorescence of $Y_3Al_5O_{12}$:Ce appears yellow while the fluorescence of $Y_3Al_2Ga_3O_{12}$:Ce appears green.

At low temperatures the fluorescence in these materials shows evidence of structure.  In Fig. 2 the fluorescence spectra of $Y_3Al_5O_{12}$:Ce, $Lu_3Al_5O_{12}$:Ce and $Y_3Al_2Ga_3O_{12}$:Ce are shown to be partially resolved into two components at $77^{\circ}$K.  The positions of the two lines are found to vary with the host.

Several additional experiments have been performed on these materials.  The lifetime of the fluorescence of $Y_3Al_5O_{12}$:Ce has been
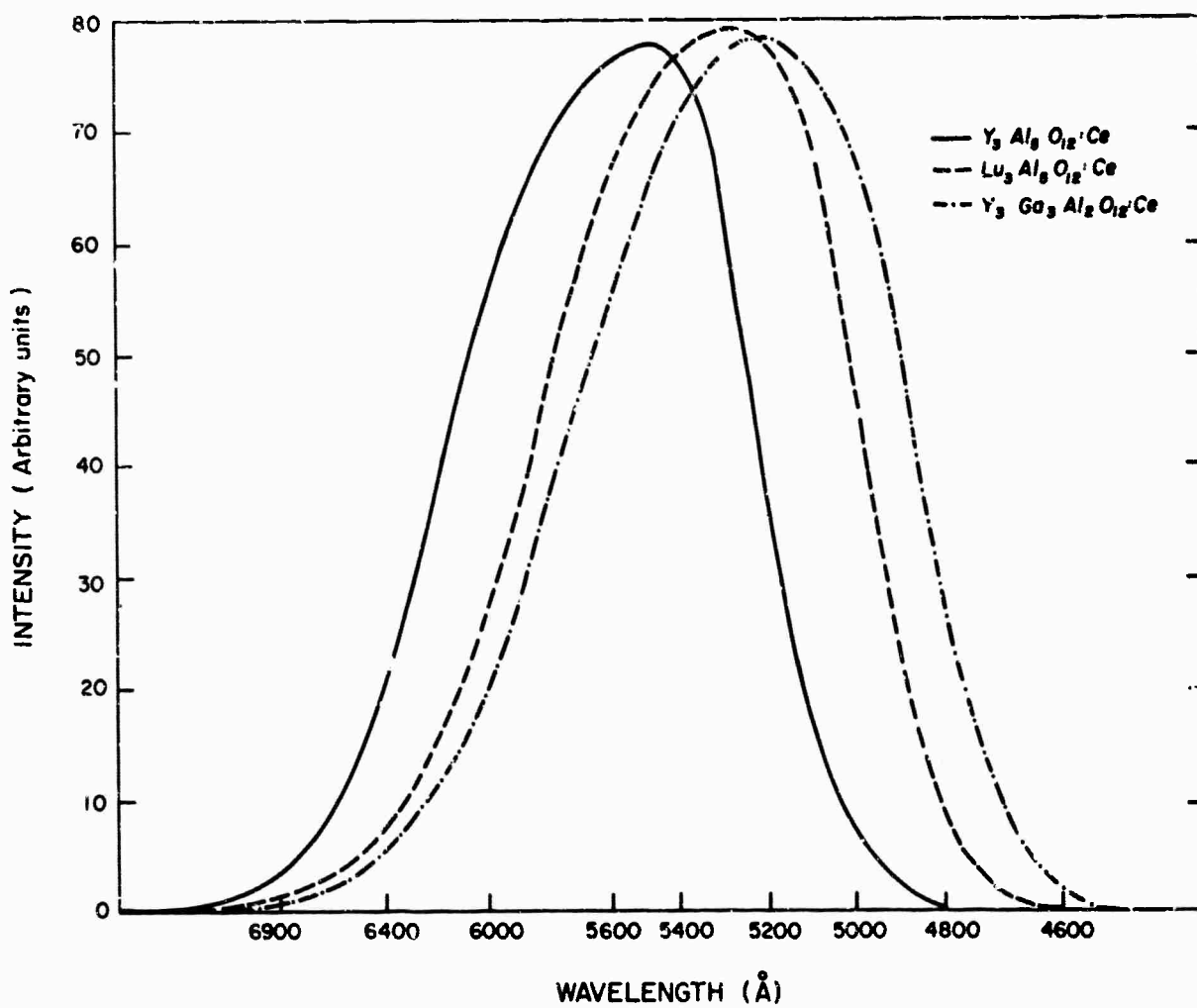
FIG. 1 Fluorescence profiles of cerium activated $Y_3Al_5O_{12}$, $Lu_3Al_5O_{12}$ and $Y_3Al_2Ga_3O_{12}$. These measurements were taken at room temperature and have not been corrected for the photomultiplier response.

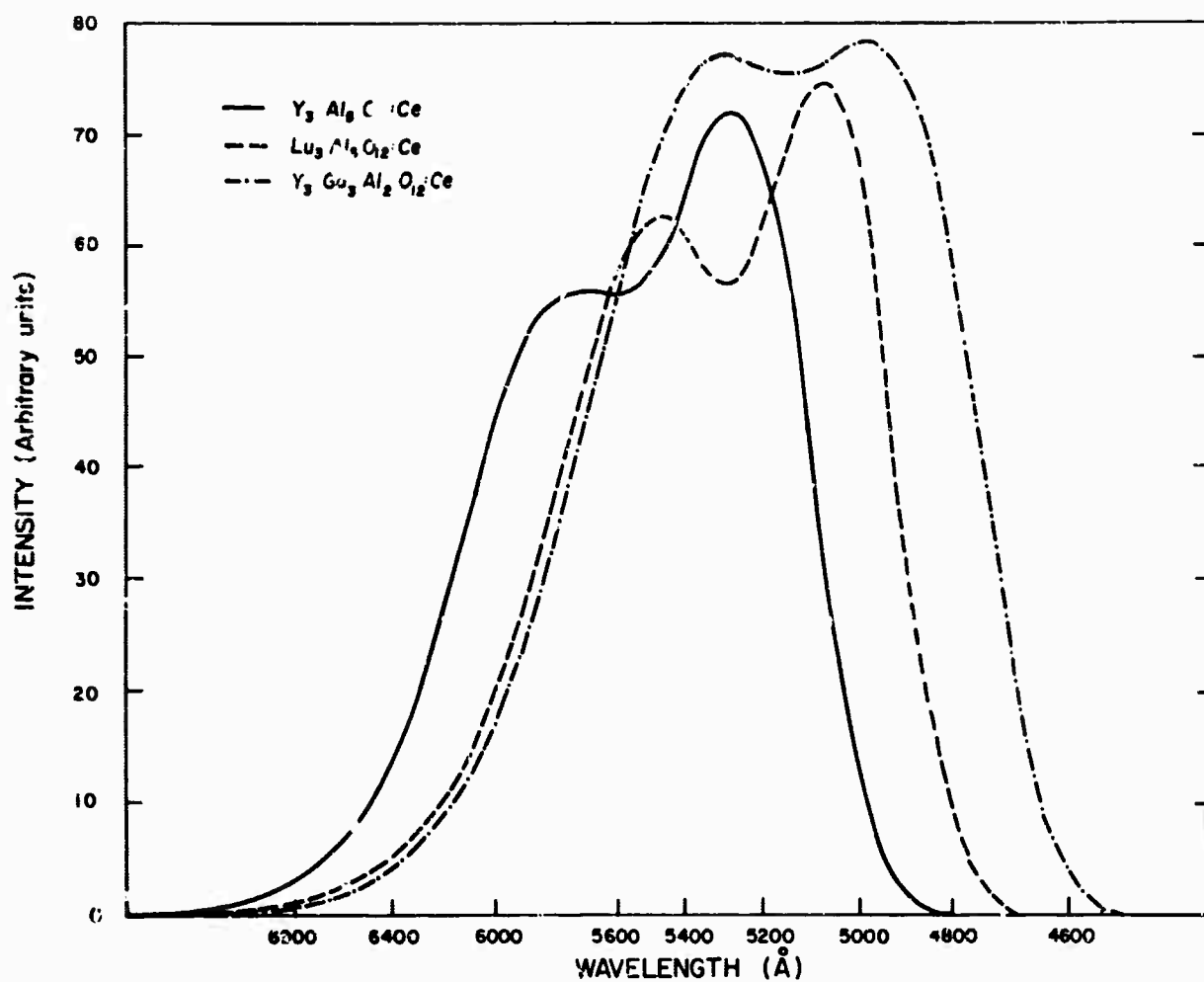FIG. 2  Fluorescence profiles of cerium activated $Y_3Al_5O_{12}$, $Lu_3Al_5O_{12}$ and $Y_3Al_2Ga_3O_{12}$ measured at $77^\circ K$.  These profiles have not been corrected for the photomultiplier response.

found to be less than 1 $\mu$sec. Fluorescence was not observed in crystals of $Y_3Ga_5O_{12}$:Ce and the fluorescence intensity in mixed crystals of the type $Y_3Al_{5-n}Ga_nO_{12}$:Ce diminished markedly for n>3. In addition, the crystals of $Y_3Al_2Ga_3O_{12}$:Ce exhibit a phosphorescence which persists for several seconds. The role of impurities taken up by the crystals from the flux has not been determined.

The absorption spectrum of $Y_3Al_5O_{12}$:Ce obtained from Czochralski-grown crystals shows two absorption bands at approximately 440 m$\mu$ and 340 m$\mu$. The flux-grown crystals of $Y_3Al_5O_{12}$:Ce showed an additional absorption band at approximately 265 m$\mu$, apparently due to the inclusion of some of the flux solvent material in the lattice. Absorption bands have been observed in the infrared at 2.6 $\mu$ and 2.8 $\mu$.

The samples used in the experiments described above were prepared by the flux solvent method.[3] The concentrations are those of the starting materials. Crystals of $Y_3Al_5O_{12}$:Ce were also prepared by the Czochralski technique[3] for comparison. The fluorescence of the crystals was excited by commercial long-wavelength uv sources. The fluorescence profiles were recorded on a Perkin Elmer Type 112 recording spectrometer. An S-20 response photomultiplier tube was used to detect the output of the spectrometer.

The rapid decay time and large linewidth of this fluorescence suggest that these bands are not the f → f transitions observed in rare earth ions. The infrared absorption bands cannot be assigned to the $Ce^{3+}$ ion, which should have one group of lines corresponding to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transitions at approximately 4.5 $\mu$. The two components observed in the low temperature fluorescence spectra of these materials may be due to the two

absorption lines showing a Stokes shift. (These results are similar to
those of Kröger and Bakker except that the apparent Stokes shift in our
materials is much larger than for the materials which they measure.) The
optical spectra do not appear to originate from the $Ce^{3+}$ ion and instead
may be due to cerium ion pairs or to a cerium ion of a different valence
or its associated compensating site. The interpretation of these data is
still incomplete and further experiments are in progress to clarify these
results.

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